

**ENVIRONMENTAL AND WASTE MANAGEMENT:
ADVANCES THROUGH THE ENVIRONMENTAL
MANAGEMENT SCIENCE PROGRAM**

Waste Treatment, Processing and Removal

Cosponsored with the Division of Analytical Chemistry

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DIVISION OF ENVIRONMENTAL CHEMISTRY

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Tuesday, March 30, 2004

Organizers: T. Zachry

Presiding: V. Kothari

Time	Paper
1:30 p.m.	Introductory Remarks.
1:35 p.m.	Actinides in Hanford tank waste simulants: Chemistry of selected species in oxidizing alkaline solutions. <u>K.L. Nash</u> , I. Laszak, M. Borkowski, M. Hancock, L. Rao and W.A. Reed
1:55 p.m.	Precipitation of scale-forming species during processing of high level wastes. <u>S.V. Mattigod</u> , D.T. Hobbs, K.E. Parker and D.E. McCready
2:15 p.m.	Modeling hydrogen generation rates in the Hanford waste treatment and immobilization plant. <u>D.M. Camaioni</u> , S.A. Bryan, R.T. Hallen, D.J. Sherwood and L.M. Stock
2:35 p.m.	Iron phosphate glasses for vitrifying DOE high priority nuclear wastes. <u>C.-W. Kim</u> and D.E. Day
2:55 p.m.	Transformation of magnetite to goethite during Cr(VI) reduction under alkaline pH conditions. <u>Y.T. He</u> and S.J. Traina
3:15 p.m.	Intermission.
3:35 p.m.	Influence of illite and kaolin on chromium(VI) reduction by sulfide. Y. Lan, C. Kim, <u>B. Deng</u> and E.C. Thornton

- 3:55 p.m. **Overcoming barriers to the remediation of carbon tetrachloride through manipulation of competing reaction mechanisms.** P.G. Tratnyek, J.E. Amonette and E.J. Bylaska
- 4:15 p.m. **Reduction of health risks due to chromium(VI) using Mesquite: A potential Cr phytoremediator.** J.L. Gardea-Torresdey, M.V. Aldrich, J. Peralta-Videa and J. Parsons
- 4:35 p.m. **Automated kinematics equations generation and constrained motion planning resolution for modular and reconfigurable robots.** F.G. Pin, L.J. Love and D.L. Jung
- 4:55 p.m. Concluding Remarks.

ABSTRACTS

Actinides in Hanford tank waste simulants: Chemistry of selected species in oxidizing alkaline solutions. Kenneth L. Nash¹, Ivan Laszak², Marian Borkowski³, Melissa Hancock², Linfeng Rao⁴ and Wendy A. Reed⁴; ¹Department of Chemistry, Washington State University, P.O. Box 644630, Pullman, WA 99364-4630, knash@wsu.edu; ²Chemistry Division, Argonne National Laboratory; ³Carlsbad Operations, Los Alamos National Laboratory; ⁴Glenn T. Seaborg Center, Chemical Sciences Division, Lawrence Berkeley National Laboratory.

To enhance removal of selected troublesome nonradioactive matrix elements (P, Cr, Al, S) from the sludges in radioactive waste tanks at the Hanford site, various chemical washing procedures have been evaluated. It is intended that leaching should leave the actinides in the residual sludge phase for direct vitrification. Oxidative treatment with strongly alkaline solutions has emerged as the best approach to accomplishing this feat. However, because the most important actinide ions in the sludge can exist in multiple oxidation states, it is conceivable that changes in actinide oxidation state speciation could interfere with hopes and plans for actinide insolubility. In this presentation, we discuss both the impact of oxidative alkaline leachants on actinide oxidation state speciation and the chemistry of oxidized actinide species in the solution phase. Actinide oxidation does occur during leaching, but the solubility behavior is complex. Mixed ligand complexes may dominate solution phase speciation of actinides under some circumstances.

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Precipitation of scale-forming species during processing of high level wastes.

Shas V. Mattigod¹, David T. Hobbs², Kent E. Parker¹ and Dave E. McCready³; ¹Pacific Northwest National Laboratory, Battelle, P.O. Box 999, MSIN K6-81, Richland, WA 99352, sv.mattigod@pnl.gov; ²Savannah River Technology Center, Westinghouse Savannah River Company; ³Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory.

High-level wastes from fuel-reprocessing operations are being evaporated at the DOE Savannah River Site to concentrate the liquids to about 30 to 40% of their original volume before they are discharged into a holding tank. Recently, the operation of one of the evaporators became progressively more difficult due to more frequent buildup of limited solubility aluminosilicate compounds resulting in the shutdown of the evaporator. Our research objectives were to identify and characterize the chemistry and microstructure of these scale-forming species and to determine the kinetics of formation and transformation of these solids under evaporator conditions. The data we obtained from these tests showed that hydroxide concentration and process temperature are the key factors that control the rate of formation and transformation of the scale forming solids such as zeolite A, sodalite and cancrinite.

Modeling hydrogen generation rates in the Hanford waste treatment and immobilization plant.

Donald M. Camaioni¹, Samuel A. Bryan¹, Richard T. Hallen¹, David J. Sherwood² and Leon M. Stock³; ¹Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, donald.camaioni@pnl.gov; ²Bechtel National, Inc.; ³Consultant.

This presentation describes a project in which Hanford Site and Environmental Management Science Program investigators addressed issues concerning hydrogen generation rates in the Hanford waste treatment and immobilization plant. The hydrogen generation rates of radioactive wastes must be estimated to provide for safe operations. While an existing model satisfactorily predicts rates for quiescent wastes in Hanford underground storage tanks, pretreatment operations will alter the conditions and chemical composition of these wastes. Review of the treatment process flowsheet identified specific issues requiring study to ascertain whether the model would provide conservative values for waste streams in the plant. These include effects of adding hydroxide ion, *alpha* radiolysis, saturation with air (oxygen) from pulse-jet mixing, treatment with potassium permanganate, organic compounds from degraded ion exchange resins and addition of glass-former chemicals. The effects were systematically investigated through literature review, technical analyses and experimental work.

Iron phosphate glasses for vitrifying DOE high priority nuclear wastes. Cheol-Woon Kim and Delbert E. Day; Department of Ceramic Engineering and the Graduate Center for Materials Research, University of Missouri-Rolla, 101 Straumanis Hall, Rolla, MO 65409-1170, Fax: 573-341-2071, cheol@umr.edu.

Iron phosphate glasses have been studied as an alternative glass for vitrifying Department of Energy (DOE) high priority wastes. The high priority wastes were the Low Activity Waste (LAW) and the High Level Waste (HLW) with high chrome content stored at Hanford, WA, and the Sodium Bearing Waste (SBW) stored at the Idaho National Engineering and Environmental Laboratory. These wastes were recommended by Tanks Focus Area since they were expected to require special attention when vitrified in borosilicate glasses. All three of these wastes have been successfully vitrified in iron phosphate glasses at waste loadings ranging from a low of 32 wt% for the high sulfate LAW to 40 wt% for the SBW to a high of 75 wt% for the high chrome HLW. In addition to these desirable high waste loadings, the iron phosphate glasses were easily melted, typically between 950 and 1200°C, in less than 4 hours in commercial refractory oxide containers. It is noteworthy that the chemical durability of both glassy and deliberately crystallized iron phosphate wasteforms not only met, but significantly exceeded, all current DOE chemical durability requirements as measured by the Product Consistency Test (PCT) and Vapor Hydration Test (VHT). The high waste loading, low melting temperature, rapid furnace throughput (short melting time) and their outstanding chemical durability could significantly accelerate the clean up effort and reduce the time and cost of vitrifying these high priority wastes.

Transformation of magnetite to goethite during Cr(VI) reduction under alkaline pH conditions. Y. Thomas He¹ and Samuel J. Traina²; ¹Environmental Science Graduate Program, Ohio State University, Columbus, OH 43210, heyong@vt.edu; ²Sierra Nevada Research Institute, University of California, Merced.

This study investigated Cr(VI) reduction by synthetic magnetite under alkaline pH conditions similar to high level wastes at the Hanford site. Cr(VI) reduction by magnetite is significantly inhibited at alkaline pH, compared to the complete sorption/reduction at acid and neutral pH. This is probably due to (1) trace amounts of O₂ in the system which depletes Fe(II) available for Cr(VI) reduction, since O₂ is much more reactive than Cr(VI) under high pH conditions and (2) a formation of a passivation layer of maghemite and/or goethite blocking the Fe²⁺ surface sites in magnetite. Our experiments showed magnetite was indeed transformed into maghemite by a well-known process. However, TEM and XRD analyses showed a prominent goethite phase was also formed and the intensity of goethite peaks in the XRD spectra increased with NaOH concentration. Goethite formation has implications for enhanced removal of metal contaminants in the tank waste through sorption processes.

Influence of illite and kaolin on chromium(VI) reduction by sulfide. Yeqing Lan¹, Chulsung Kim², Baolin Deng³ and Edward C. Thornton⁴; ¹College of Sciences, Nanjing Agricultural University, Nanjing 210095, China, yqlan102@yahoo.com; ²Department of Chemistry, Rainy River Community College; ³Department of Civil and Environmental Engineering, University of Missouri-Columbia, Columbia, MO 65211, Fax: 573-882-4784, dengb@missouri.edu; ⁴Field Hydrology and Chemistry Group, Pacific Northwest National Laboratory.

Use of hydrogen sulfide for reductive chromate immobilization requires us to understand how the minerals in the subsurface environment will affect the reaction. In this study, we examined the effects of illite and kaolin on the reduction of Cr(VI) by hydrogen sulfide under the anaerobic condition at pH ranging from 7.67 to 9.07. The results showed that extremely low concentration of iron dissolved from illite could greatly accelerate the rate of Cr(VI) reduction. An electron cycling process between Fe(II)/Fe(III) was believed to be responsible for the catalysis. The effect of iron could be completely blocked by phenanthroline that formed a strong complex with Fe(II). Elemental sulfur produced as a reaction product was also able to catalyze the reaction in the heterogeneous system. In the kaolin suspension, however, the effect of elemental sulfur could be completely eliminated because of the adsorption of elemental sulfur by kaolin.

Overcoming barriers to the remediation of carbon tetrachloride through manipulation of competing reaction mechanisms. Paul G. Tratnyek¹, James E. Amonette² and Eric J. Bylaska³; ¹Department of Environmental and Biomolecular Systems, Oregon Health & Science University, 20000 NW Walker Road, Beaverton, OR 97006, Fax: 503-748-1273, tratnyek@ese.ogi.edu; ²Pacific Northwest National Laboratory; ³Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory.

Most approaches that have been proposed for the remediation of groundwater contaminated with carbon tetrachloride produce chloroform as the major product and methylene chloride as a minor product. Both of these products are nearly as persistent and problematic as the parent compound, but competing reaction pathways produce the more desirable products carbon monoxide and/or formate. Branching between these reaction pathways is highly variable, but the controlling factors have not been identified. To improve the applicability of reductive remediation technologies to the large plumes of carbon tetrachloride at several DOE sites, we are pursuing the complete characterization of the mechanisms and kinetics of competing degradation reactions of carbon tetrachloride through laboratory experiments closely coordinated with theoretical modeling studies. The results are beginning to suggest strategies for maximizing the yield of desirable products from carbon tetrachloride degradation, which will be tested in column model systems using real site waters and matrix materials.

Reduction of health risks due to chromium(VI) using Mesquite: A potential Cr phytoremediator. Jorge L. Gardea-Torresdey¹, Mary V. Aldrich², Jose Peralta-Videa¹ and Jason Parsons²; ¹Department of Chemistry, University of Texas at El Paso, 500 West University Ave., El Paso, TX 79968-0513, Fax: 915-747-5748, jgardea@utep.edu; ²Environmental Science and Engineering Ph.D. Program, University of Texas at El Paso.

Chromium is a transition metal extensively used in industry. Cr mining and industrial operations account for chromium wastes at Superfund sites in the United States. A study was performed to investigate the possibility of using mesquite (*Prosopis spp.*), which is an indigenous desert plant species, to remove Cr from contaminated sites. In this study, mesquite plants were grown in an agar-based medium containing 75 mg L⁻¹ and 125 mg L⁻¹ of Cr(VI). The Cr content of leaf tissue (992 mg kg⁻¹ of dry weight, from 125 mg L⁻¹ of Cr(VI)) indicated that mesquite could be classified as a chromium hyperaccumulator. X-ray absorption spectroscopy (XAS) studies performed to experimental samples showed that mesquite roots absorbed some of the supplied Cr(VI). However, the data analyses of plant tissues demonstrated that the absorbed Cr(VI) was fully reduced to Cr(III) in the leaf tissue.

Automated kinematics equations generation and constrained motion planning resolution for modular and reconfigurable robots. François G. Pin, Lonnie J. Love and David L. Jung; Robotics and Energetics Group, Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6305, Fax: 865-574-4624, pinfg@ornl.gov.

Contrary to the repetitive tasks performed by industrial robots, the tasks in most DOE missions such as environmental restoration or Decontamination and Decommissioning (D&D) can be characterized as “batches-of-one”, in which robots must be capable of adapting to changes in constraints, tools, environment, criteria and configuration. No commercially available robot control code is suitable for use with such widely varying conditions. In this talk we present our development of a “generic code” to allow real time (at loop rate) robot behavior adaptation to changes in task objectives, tools, number and type of constraints, modes of controls or kinematics configuration. We present the analytical framework underlying our approach and detail the design of its two major modules for the automatic generation of the kinematics equations when the robot configuration or tools change and for the motion planning under time-varying constraints. Sample problems illustrating the capabilities of the developed system are presented.